

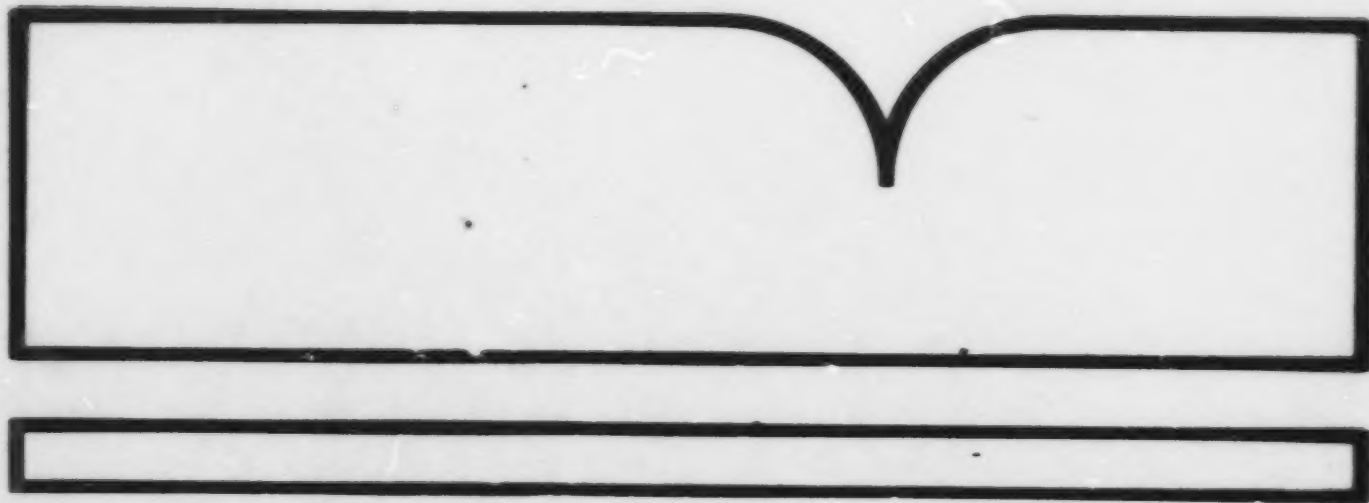
Technical Assistance for  
Huntington Park Group Treatment Facility

Centec Corp., Reston, VA

Prepared for

Environmental Protection Agency, Cincinnati, OH

Jun 85



EPA/600/2-85/078  
June 1985

TECHNICAL ASSISTANCE FOR  
HUNTINGTON PARK GROUP TREATMENT FACILITY

by

Donald S. Harrison  
CENTEC Corporation  
Reston, VA 22090

Contract No. 68-03-2907-17

Project Officer

Alfred B. Craig  
Nonferrous Metals and Minerals Branch  
Industrial Environmental Research Laboratory  
Cincinnati, OH 45268

HAZARDOUS WASTE ENGINEERING RESEARCH LABORATORY  
OFFICE OF RESEARCH AND DEVELOPMENT  
U.S. ENVIRONMENTAL PROTECTION AGENCY  
CINCINNATI, OH 45268

REPRODUCED BY  
NATIONAL TECHNICAL  
INFORMATION SERVICE  
U.S. DEPARTMENT OF COMMERCE  
SPRINGFIELD, VA. 22161

| TECHNICAL REPORT DATA<br>(Please read Instructions on the reverse before completing)                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            |                                                             |                                                   |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------|---------------------------------------------------|
| 1. REPORT NO.<br>EPA/600/2-85/078                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               | 2.                                                          | 3. RECIPIENT'S ACCESSION NO.<br>PDB 5 2 22768 /75 |
| 4. TITLE AND SUBTITLE<br>Technical Assistance for Huntington Park Group<br>Treatment Facility                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   | 5. REPORT DATE<br>June 1985                                 |                                                   |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 | 6. PERFORMING ORGANIZATION CODE<br>US EPA/IERL-Ci/IPCD      |                                                   |
| 7. AUTHOR(S)<br>Donald S. Harrison                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              | 8. PERFORMING ORGANIZATION REPORT NO.                       |                                                   |
| 9. PERFORMING ORGANIZATION NAME AND ADDRESS<br>Centec Corporation<br>11260 Roger Bacon Drive<br>Reston, VA 22090                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                | 10. PROGRAM ELEMENT NO.                                     |                                                   |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 | 11. CONTRACT/GRANT NO.<br>Contract 68-03-2907               |                                                   |
| 12. SPONSORING AGENCY NAME AND ADDRESS<br>Hazardous Waste Engineering Research Laboratory<br>Office of Research & Development<br>U.S. Environmental Protection Agency<br>Cincinnati, OH 45268                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   | 13. TYPE OF REPORT AND PERIOD COVERED<br>Final Report       |                                                   |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 | 14. SPONSORING AGENCY CODE<br>EPA/600/12                    |                                                   |
| 15. SUPPLEMENTARY NOTES                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         |                                                             |                                                   |
| 16. ABSTRACT<br><p>In 1980 a preliminary study of the group treatment concept was conducted at a number of plating firms within Huntington Industrial Park, Providence, Rhode Island. That earlier (1980) effort found that, with ten participating firms, substantial savings could be realized. This report is a follow-up to the 1980 study.</p> <p>The work described herein investigated the 1982 status of pollution control in Huntington Industrial Park through three case studies. The studies revealed that these plants were either meeting or showed promise of meeting 1982 pretreatment regulations on levels of cyanides and heavy metals. This was achieved through in-plant changes to reduce water consumption, installation of recovery equipment, and elimination of cyanide process solutions. In some cases, the installation of electrolytic recovery systems eliminated the need for expensive treatment equipment, the generation of metallic hydroxide sludge, and associated disposal problems.</p> |                                                             |                                                   |
| 17. KEY WORDS AND DOCUMENT ANALYSIS                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             |                                                             |                                                   |
| a. DESCRIPTORS                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  | b. IDENTIFIERS/OPEN ENDED TERMS                             | c. COSATI Field Group                             |
| Metal Finishing<br>Waste Treatmeant<br>Solid Waste<br>Metals Removal<br>Centralized Waste Treatment                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             | Electroplating<br>Wastewater<br>Pollution Control<br>Sludge |                                                   |
| 18. DISTRIBUTION STATEMENT<br>Unrestricted                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      | 19. SECURITY CLASS (This Report)<br>Unrestricted            | 21. NO. OF PAGES<br>59                            |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 | 20. SECURITY CLASS (This page)<br>Unrestricted              | 22. PRICE<br>\$10.00                              |

#### DISCLAIMER

This report has been reviewed by the Industrial Environmental Research Laboratory, U.S. Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the U.S. Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

## FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory-Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report is a follow-up to a previously published report, "Group Treatment Evaluation for Metal Finishers" (EPA 600/8-81-143). The earlier report covered the period February to June 1980. The purpose of the earlier effort was to conduct a preliminary study of the concept of centralized waste treatment as applied to the electroplating firms within Huntington Industrial Park, Providence, Rhode Island. The report described herein provides data taken two years later from three of the ten original plants studied. It has been demonstrated that these plants are either meeting or show promise of meeting the pretreatment regulations (in effect at the time of this writing) on levels of cyanides and heavy metals.

David G. Stephan  
Director  
Industrial Environmental Research Laboratory  
Cincinnati

## ABSTRACT

In 1980 a preliminary study of the group treatment concept was conducted at a number of plating firms within Huntington Industrial Park, Providence, Rhode Island. That earlier (1980) effort found that, with ten participating firms, substantial savings could be realized. This report is a follow-up to the 1980 study.

The work described herein investigated the 1982 status of pollution control in Huntington Industrial Park through three case studies. The studies revealed that these plants were either meeting or showed promise of meeting 1982 pretreatment regulations on levels of cyanides and heavy metals. This was achieved through in-plant changes to reduce water consumption, installation of recovery equipment, and elimination of cyanide process solutions. In some cases, the installation of electrolytic recovery systems eliminated the need for expensive treatment equipment, the generation of metallic hydroxide sludge, and associated disposal problems.

## CONTENTS

|                                                          |     |
|----------------------------------------------------------|-----|
| FOREWORD.....                                            | iii |
| ABSTRACT.....                                            | iv  |
| FIGURES AND TABLES.....                                  | vi  |
| ACKNOWLEDGEMENT.....                                     | vii |
|                                                          |     |
| 1.0 INTRODUCTION.....                                    | 1   |
| 2.0 CONCLUSIONS AND RECOMMENDATIONS.....                 | 5   |
| 3.0 CASE STUDIES.....                                    | 6   |
|                                                          |     |
| CASE NO. 1 - PLANT NO. 1.....                            | 8   |
| CASE NO. 2 - PLANT NO. 4.....                            | 18  |
| CASE NO. 3 - PLANT NO. 10.....                           | 22  |
|                                                          |     |
| REFERENCES.....                                          | 33  |
| APPENDICES                                               |     |
| A. ANALYTICAL RESULTS OF PLANT SURVEY - 1982.....        | 34  |
| B. ANALYTICAL RESULTS OF PLANT SURVEY - 1980.....        | 43  |
| C. GUIDELINES FOR BATCH TREATMENT OF DUMP SOLUTIONS..... | 48  |

## FIGURES

| <u>Number</u> |                                                    | <u>Page</u> |
|---------------|----------------------------------------------------|-------------|
| 1.            | Plant No. 1 - Typical Electrolytic Recovery System | 12          |
| 2.            | Plant No. 1 - Plating Process Cleaning Solution    | 14          |
| 3.            | Plant No. 1 - Batch pH Control System              | 16          |
| 4.            | Automatic Plating Machine Process Sequence         | 26          |

## TABLES

| <u>Number</u> |                                                                                         | <u>Page</u> |
|---------------|-----------------------------------------------------------------------------------------|-------------|
| 1.            | Huntington Industrial Park Plant Effluent Flow Rates February, 1980                     | 7           |
| 2.            | Plant No. 1 - Performance Comparison Effluent Analysis February 1980 and February 1982  | 9           |
| 3.            | Plant No. 4 - Performance Comparison Effluent Analysis February 1980 and February 1982  | 19          |
| 4.            | Plant No. 10 - Performance Comparison Effluent Analysis February 1980 and February 1982 | 23          |
| 5.            | Plant No. 10 - Field Data - Dragout Experiment                                          | 25          |
| 6.            | Sources of Cyanide Pollution                                                            | 30          |

#### ACKNOWLEDGEMENT

The authors wish to acknowledge the considerable assistance provided by Mr. Eric W. Salomon, Lang Jewelry Company in Providence, Rhode Island, in providing information and facilitating data collection.

## SECTION 1

### INTRODUCTION

The Huntington Industrial Park in Providence, Rhode Island presents a unique situation for studying pretreatment of wastes from electroplating operations. No other area of comparable size has such a high concentration of electroplating firms. The jewelry industry is heavily represented in the Park. The Narragansett Bay Water Quality Management District Commission Treatment Plant which serves the Providence area receives large concentrations of metals from the industrial park's effluent. In 1980 it was determined that as much as \$30,000 worth of silver was discharged into Narragansett Bay per week.

Huntington Industrial Park is located within Providence at the Cranston, Rhode Island boundary. With easy access to highways, the park is ideally located in respect to the many electroplating and jewelry firms in the area. Although not planned as an electroplating center when constructed ten years ago, Huntington Industrial Park now contains at least eleven plating operations. With the exception of one plating job shop and one electronics concern, all are in the business of jewelry manufacturing. The number of employees within the eleven firms ranges from 25 to 350.

These plants are faced with the problem of compliance with environmental regulations<sup>1</sup>. Because of their proximity, the possibility for reducing waste treatment costs through group treatment was investigated. Group treatment, refers to the joint establishment of a waste treatment facility by a group of shops in close proximity, discharging similar wastes. Ownership, management, and operation generally involves the participating companies themselves, although a number of variants are possible. The Group Treatment Facility (GTF),

while primarily intended for the benefit of its members, can also treat the wastes of other small shops having similar waste constituents.

In early 1980, CENTEC Corporation performed a preliminary study to investigate the concept of group treatment and its application at Huntington Industrial Park (See EPA-600/82-81-143). Wastewater from each of the 10 potential participants was sampled, analyzed, and flows were measured. A mathematical model was used to size and cost the GTF and to indicate the economic decision for each of the participants. Transportation of wastes by both truck and by private sewer system was evaluated. Preliminary contacts were made with Small Business Association, State of Rhode Island Department of Environmental Management, Providence Department of Public Works, Rhode Island Department of Economic Development, and the Bank of Wisconsin (a potential underwriter). As a result of the earlier feasibility study's conclusion that the proposed GTF was feasible and might result in savings, the potential participants decided to move ahead with the project<sup>3</sup>.

The Group Treatment Facility design completed under the earlier study called for each plant to install countercurrent rinsing and initiate other innovative techniques to minimize the volume of rinse water requiring shipment to the GTF. Each plant was required to achieve flow reductions of 60 to 90 percent.

It was also determined that the treatment of cyanides would be the most costly GTF process. The preliminary study concluded that if cyanides could be eliminated from the plants' production processes, the need for a joint treatment facility would have to be reevaluated.

Since that 1980 study, most of the plants in the park have instituted the recommended in-plant changes to significantly reduce the volumes of wastewater

being treated. In addition, and perhaps of most significance, many plants have replaced some cyanide baths and cleaners with non-cyanide types while retaining product quality.

The three-case study project described in this report had as its objective the evaluation of the changes made by the platers at Huntington Park since the original study, and the reevaluation of the course of action needed to achieve compliance in light of those changes.

## SECTION 2

### CONCLUSIONS AND RECOMMENDATIONS

The three case studies in this report dramatically demonstrate the ability of plating shops in the Huntington Park area to meet pretreatment regulations with minimal capital investment. In most cases, the purchase of wastewater treatment can be limited to a relatively simple pH adjustment system for treating batch dumps prior to discharge.

Application of the techniques employed by the three plants studied to other plants in the Park will eliminate the need for a Group Treatment Facility. In particular, the utilization of electrolytic recovery units can often eliminate the need for treatment equipment and avoid the generation of hydroxide sludges and their disposal problems.

### SECTION 3

#### CASE STUDIES

Data collected in the 1980 study of 10 plants in Huntington Industrial Park showed a wide range of effluent flow rates (Table 1). Initial contacts with plant personnel during the current project revealed that substantial in-plant changes aimed at reducing pollutants and wastewater volume had been implemented as a result of the 1980 study. Three plants were selected and agreed to cooperate in case studies as examples of achievements possible with minimal capital outlay. Technical assistance was provided in cases where additional reduction of pollutants and wastewater volume was identified.

Table 1. Huntington Industrial Park  
Plant Effluent Flow Rates  
February 1980

| <u>Plant No.</u> | <u>Effluent Flow Rate, gpd</u> |
|------------------|--------------------------------|
| 1                | 64,000                         |
| 2                | 24,700                         |
| 3                | 47,400                         |
| 4                | 32,000                         |
| 5                | 60,900                         |
| 6                | 31,300                         |
| 7                | 6,000                          |
| 8                | 13,500                         |
| 9                | 4,300                          |
| 10               | 48,600                         |

## CASE NO. 1 - PLANT NO. 1

Plant No. 1 operates a plating process to apply finishes of copper, nickel, silver, gold, and rhodium to a variety of jewelry products. The engineering survey of Plant No. 1 was conducted on February 17, 1982 to assess the plant's ability to comply with EPA pretreatment regulations. A comparison with plant operation observed during the February 1980 survey (Table 2) revealed that water consumption had been reduced 62.5 percent. Total regulated metals discharged were reduced 12.7 percent. Cyanides were reduced 98.2 percent. Since the previous survey, installation of countercurrent rinsing, aerating rinse-water flow restrictors, electrolytic recovery units, and the utilization of non-cyanide baths have been implemented. Analytical results of the composite effluent sample indicated that the plant is currently meeting the regulations without the need for further in-plant changes or the installation of additional treatment equipment.

The results from the plant survey define pollution levels associated with routine production of plated jewelry and do not reflect the special problems presented by the disposal of spent solutions. The volume of these "dump" solutions is very small when compared to the plant wastewater flow. A small, relatively inexpensive batch treatment system designed for this purpose is discussed in detail later in this section.

### IN-PLANT CHANGES

Wastewater volumes have been reduced 62.5 percent through the use of counter-flow rinses and the installation of flow restrictors. The flow restrictor in use at this plant is of a venturi design and mixes air with the incoming fresh water. The resulting bubbles increase the agitation in the rinse tank,

Table 2. Plant No. 1 Performance Comparison Effluent Analysis  
February 1980 and February 1982

| Parameter          | 2/80   | 2/82   | Percent Reduction |
|--------------------|--------|--------|-------------------|
| Effluent Flow, gpd | 64,000 | 24,000 | 62.5              |
| Analyses, mg/l     |        |        |                   |
| All Metals         | 1.74   | 4.05   | 12.7              |
| CN <sub>t</sub>    | 2.9    | 0.14   | 98.2              |
| Au                 | *      | <0.5   | -                 |
| Rh                 | *      | <0.5   | -                 |
| Ag                 | <0.01  | 0.05   | -                 |
| Cd                 | <0.01  | <0.01  | -                 |
| Cr <sub>t</sub>    | 0.05   | 0.22   | -                 |
| Cu                 | 0.68   | 1.04   | -                 |
| Ni                 | 0.95   | 2.56   | -                 |
| Pb                 | <0.001 | 0.007  | -                 |
| Zn                 | 0.06   | 0.17   | -                 |
| Sn                 | *      | <1.0   | -                 |

\*not analyzed

Dragout Experiment Results: DRAGOUT = 0.020 1/rack

providing better rinsing of the parts being processed.

As an added precaution against indiscriminate waste of water, a flowmeter was installed in the plant discharge line. A meter showing the instantaneous fresh water flowrate was also installed in the plating manager's office.

Approximately \$5000 was spent for in-plant changes to reduce water consumption. An annual savings of \$12,150 in water and sewer charges has been realized as a result.

Cyanides in rinses have been reduced 98.2 percent by attacking the problem at its source, the process solutions. Activators and plating solutions have been replaced with non-cyanide acidic types wherever possible.

Of particular significance in this plant are six electrolytic recovery units (Figure 1). The system consists of a small dragout tank mounted on the front (operator side) of a plating tank. The solution from the dragout tank is continuously recirculated through an electrolytic recovery cell where the plated metal is removed. Racks of parts are placed in the dragout tank prior to entry into the rinse tanks. The electrolytic cell maintains the metal concentration of the dragout tank at a very low level. The cells containing the recovered metal are replaced on a regular schedule. These systems are currently employed on the copper, nickel, gold, and rhodium plating tanks. The electrolytic recovery units are leased from Royal Recovery Systems, Plainfield, New Jersey. A monthly rental fee includes servicing of the units. A credit is given to the leasor for metals recovered from the cells.

This plant estimates an annual cost of \$10,000 for rental, service, and electricity for the electrolytic recovery units. Although little credit is received for recovered copper and nickel, the use of the units makes the

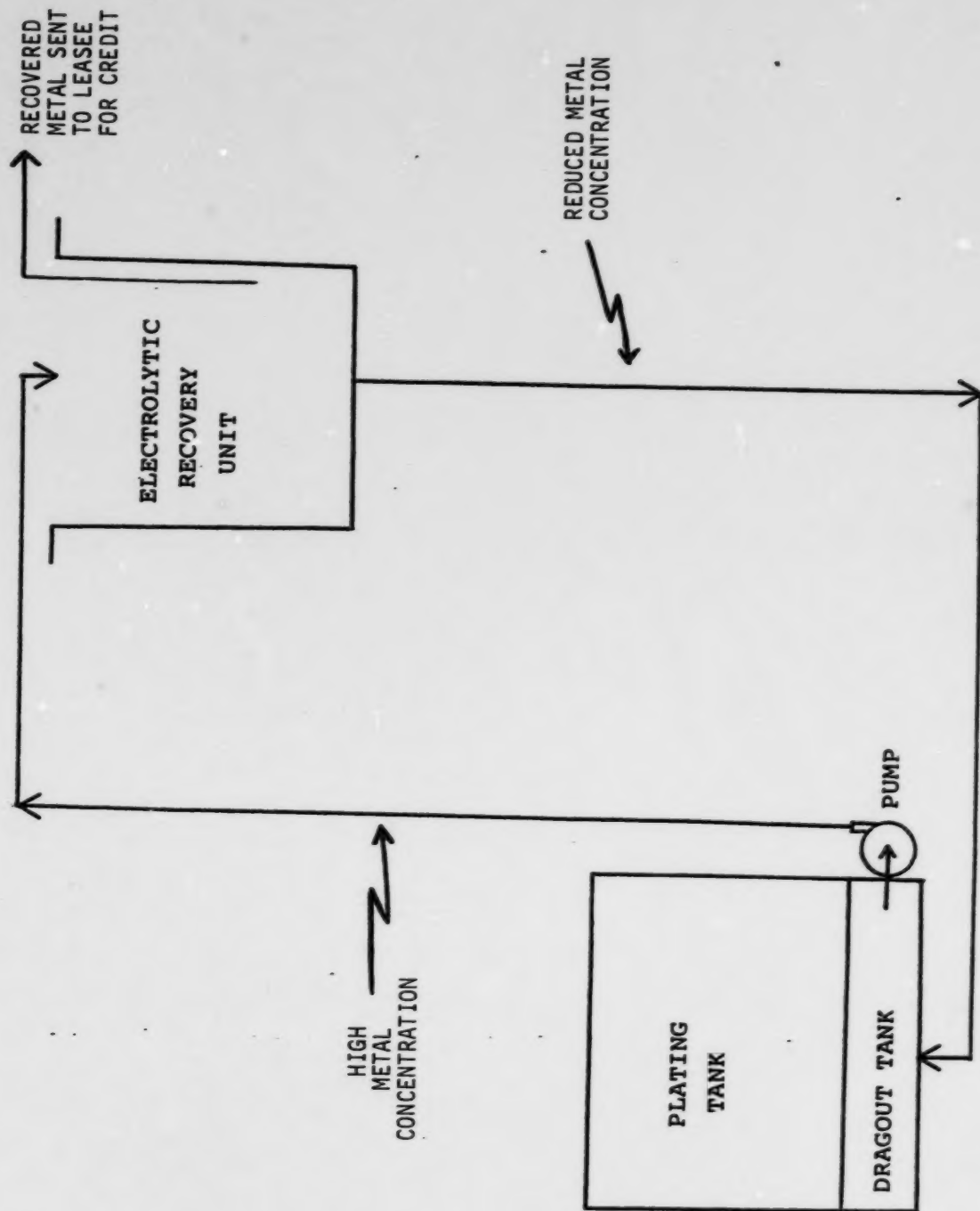


Figure 1. Typical Electrolytic Recovery System - Plant No. 1

capital investment for wastewater treatment equipment for heavy metals removal unnecessary. In addition, the electrolytic removal of the metals avoids the generation of metal hydroxide sludge and its attendant disposal problems.

#### Rinsewater Reuse

A further reduction in water consumption was realized through rinsewater reuse in the cleaning section of the plating operation.

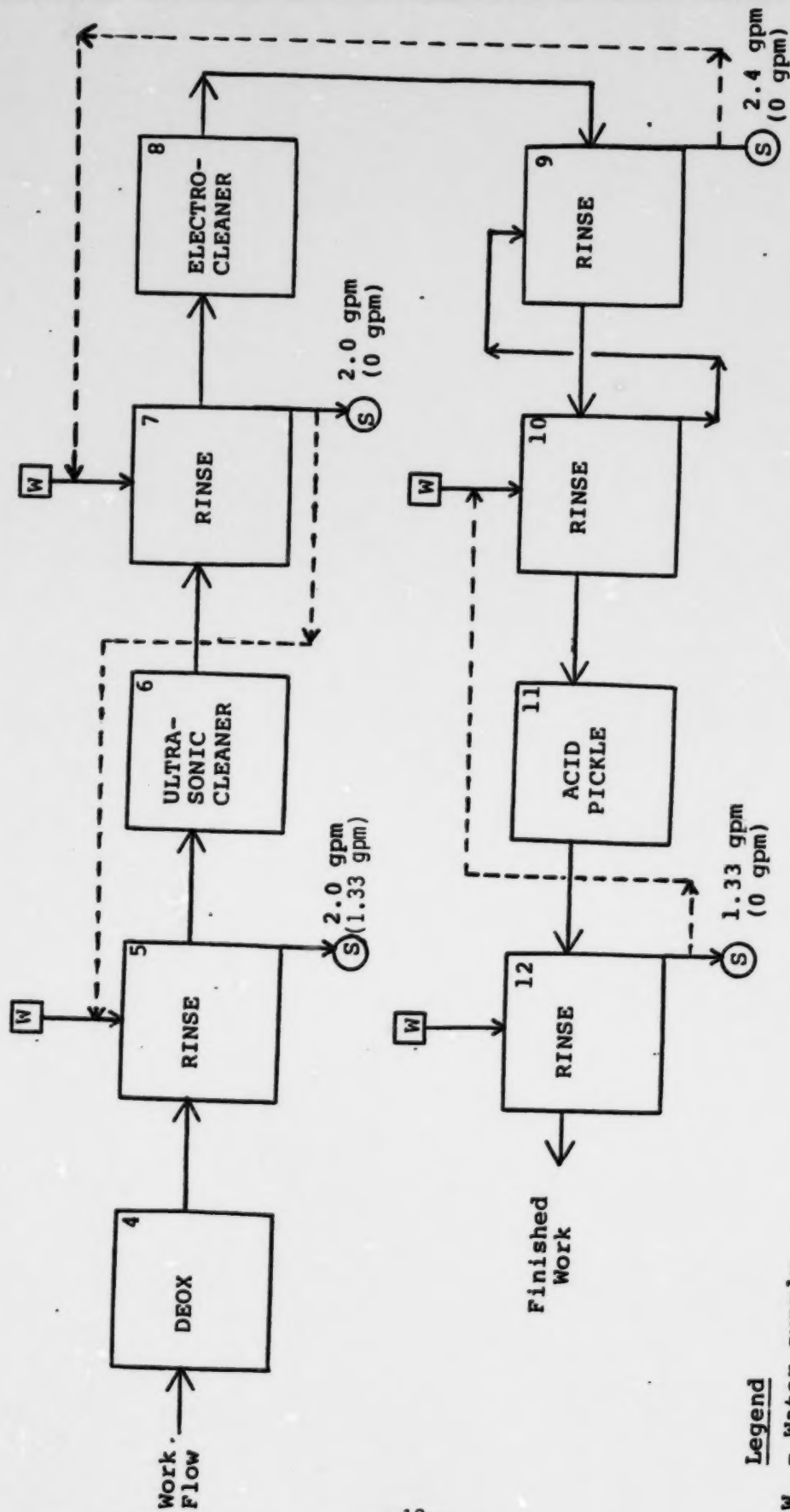
The concept of counterflow rinsing to reduce water consumption has become a common practice in electroplating operations. Installation of a two-tank counterflow rinse system to replace two overflow rinses can produce the same cleanliness with a 50 percent water reduction.

Plants utilizing counterflow rinses can achieve further water reductions by reusing rinsewater. The principle is illustrated on Figure 2 as applied to the cleaning line at Plant No. 1. The total flow of rinsewater in this section of the plant was measured during the plant survey.

Repiping the rinsewater as shown by the dotted lines (in Figure 2) will result in a water reduction of 3072 gallons per 8-hour shift. The reuse of this water is possible for the following reasons:

1. Rinse No. 12 will be acidic because of the dragout from Tank No. 11. Its acidic nature will actually provide a neutralizing effect on any caustic cleaner in Tank No. 10.
2. Since ultrasonic cleaners and electrocleaners are both caustic in nature, the resulting increase in concentration in rinse Tank No. 7 can be tolerated.
3. Supplying rinse Tank No. 5 with rinse overflow from Tank No. 7 will aid in neutralizing the acidic dragout from the deox solution thereby prolonging the life of the ultrasonic cleaner.

Repiping rinsing systems in this way requires that an elevation gradient be



Potential water savings = 6.40 gpm  
or 3072 gal/8-hr shift

Figure 2. Plant No. 1 - Plating Process - Cleaning Section

maintained from Tank No. 12 to Tank No. 5. If physical restrictions prevent elevating the tanks, transfer pumps can be installed to provide the driving force.

These principles of water reuse are also applicable to other rinses in the plating line. Caution should be exercised so that impurities in the water being reused are compatible with the process tank following the rinse tank. Acidic waters must be avoided in rinse tanks following cyanide plating.

#### Batch Dumps

The installation of electrolytic recovery units and substitution of non-cyanide solutions at Plant No. 1 eliminates the need for a conventional treatment systems. However, the periodic dumping of alkali cleaners and acid solutions requires some special handling. Two options are available for consideration:

1. Caustics and acids can be stored and bled into the plant waste stream to control the pH of the effluent (Figure 3). One bleed stream flow is set manually; the other is controlled automatically. Additional purchased caustic or acid is normally required to maintain the pH of the effluent within regulated limits. Storage tanks of sufficient size to accept the scheduled dumps are required. Careful scheduling of dumps can keep tank size to a minimum. An automatic pH control system is required to maintain the preset pH value.
2. A common dump storage tank can be utilized to collect the caustic and acid solutions. This arrangement is preferable since the storage tank can act as a buffer to sudden changes in pH. As in Option No. 1 the scheduling of dumps is important. Staggering of dumps can minimize fluctuations of pH in the storage tank thereby making control of the plant effluent easier. As in Option No. 1, purchased acid or caustic may be required.

#### Dragout Determination

Many calculations involving rinsing of plated parts or recovery of metals requires a determination of the quantity process solution clinging to the parts

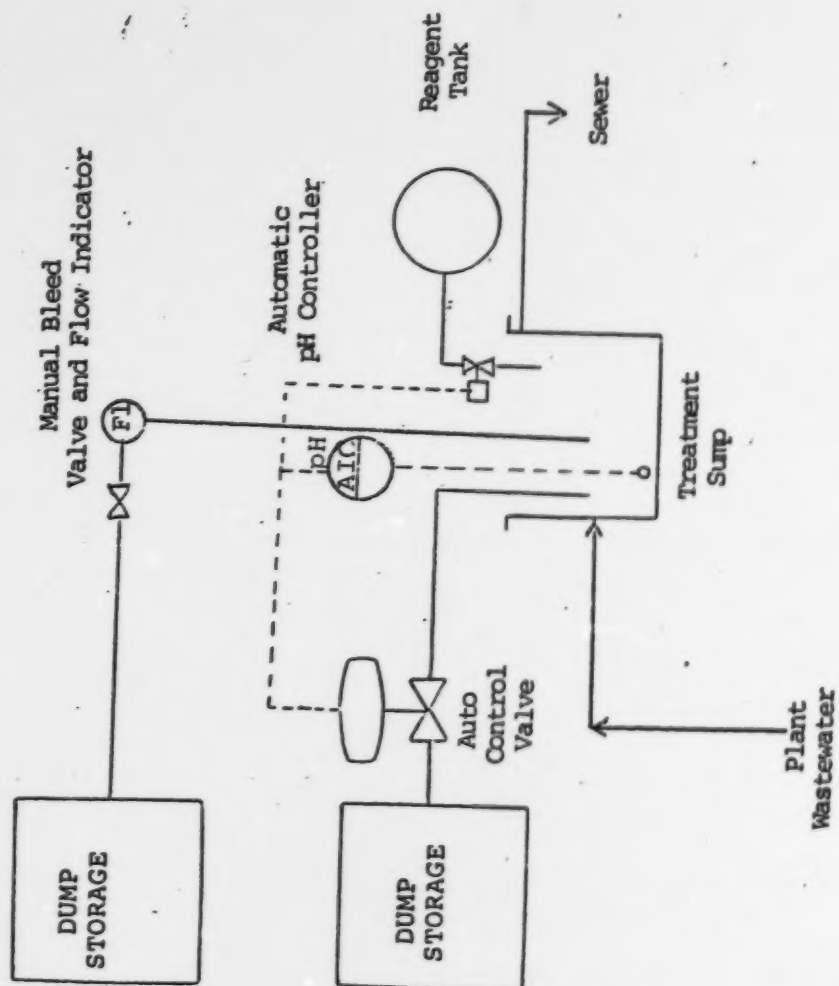


Figure 3 Plant #1 Batch pH Control System

and rack, the so-called "dragout". To determine a reasonable dragout for Plant No. 1, an experiment was conducted. The first rinse tank following the nickel plating tank was emptied, thoroughly cleaned, and refilled with fresh water. An initial sample from the rinse tank was analyzed for nickel concentration. Additional samples of the "dead" rinse tank were analyzed after 30, 60, and 90 racks had passed through the tank. A sample of the nickel plating tank was also analyzed for nickel concentration (see Appendix A for results). From these analyses, the dragout was calculated to be 0.020 liters per rack.

#### CASE NO. 2 - PLANT NO. 4

Plant No. 4 operates a plating process to apply finishes of copper, nickel, silver, gold, and rhodium to a variety of products. The engineering survey of Plant No. 4 was conducted on February 18, 1982 to assess the plant's ability to comply with EPA pretreatment regulations. A comparison with plant operation observed during the February 1980 survey (Table 3) revealed that water consumption had been reduced by 64.5 percent. Total regulated metals discharged were reduced 82.3 percent. Installation of countercurrent rinsing, aerating rinsewater flow restrictors, electrolytic recovery units, and utilization of non-cyanide baths has been implemented since the previous survey. Analytical results of the composite effluent sample indicate that the plant is currently meeting the regulations without the need for further in-plant changes or the installation of additional treatment equipment.

The results from the plant survey define pollution levels associated with routine production of plated jewelry and do not reflect the special problems presented by the disposal of spent solutions. The volume of these "dump" solutions is very small when compared to the plant wastewater flow. At the time of the survey, this plant was awaiting delivery of equipment for treatment of batch dumps.

Wastewater volumes have been reduced 64.5 percent through the use of counter-flow rinses and the installation of flow restrictors. The flow restrictor in use at this plant is also of the venturi design which mixes air with the incoming fresh water.

Cyanides in the effluent from this plant have been reduced 97.0 percent through the substitution of cyanide activators with acidic types. Cyanide

Table 3. Plant No. 4 Performance Comparison

Effluent Analysis

February 1980 and February 1982

| Parameter          | 2/80   | 2/82   | Percent Reduction |
|--------------------|--------|--------|-------------------|
| Effluent Flow, gpd | 32,000 | 11,371 | 64.5              |
| Analyses, mg/l     |        |        |                   |
| All Metals         | 1.85   | 1.69   | 82.3              |
| CN <sub>t</sub>    | 3.9    | 0.60   | 97.0              |
| Au                 | *      | <0.5   | -                 |
| Rh                 | *      | <0.5   | -                 |
| Ag                 | 0.13   | <0.01  | -                 |
| Cd                 | <0.01  | <0.01  | -                 |
| Cr <sub>t</sub>    | <0.05  | <0.05  | -                 |
| Cu                 | 0.45   | 0.33   | -                 |
| Ni                 | 1.10   | 0.70   | -                 |
| Pb                 | 0.004  | 0.006  | -                 |
| Zn                 | 0.17   | 0.06   | -                 |
| Sn                 | *      | <1.0   | -                 |

\*not analyzed

Dragout Experiment Results: DRAGOUT = 0.020 1/rack

plating solutions have been replaced wherever possible. Precious metals are recovered electrolytically.

#### Rinsewater Reuse

The possibility of further reduction in water consumption exists through reuse of rinsewater in the cleaning section of the plating operation, as discussed earlier for Plant No. 1.

#### Batch Dumps

When the survey was conducted, Plant No. 4 was expecting delivery of storage tanks and associated equipment for the pH adjustment of batch dumps of cleaners and acid solutions. Blending techniques designed to reduce the purchase of treatment chemicals were discussed with plant personnel.

#### Dragout Determination

Many calculations involving rinsing of plated parts or recovery of metals require a determination of the quantity process solution clinging to the parts and rack, the so-called "dragout". To determine a reasonable dragout for Plant No. 4, an experiment was conducted. The first rinse tank following the nickel plating tank was emptied, thoroughly clean, and refilled with fresh water. An initial sample from the rinse tank was analyzed for nickel concentration. Additional samples of the "dead" rinse tank were analyzed after 10, 27, and 40 racks had passed through the tank. A sample of the nickel plating tank was also analyzed for nickel concentration (see Appendix A for results). From these analyses, the dragout was calculated to be 0.020 liters per rack.

### CASE STUDY NO. 3 - PLANT NO. 10

The majority of the plating production from Plant No. 10 is produced on two automatic plating machines, one of which was in use during the plant survey.

The engineering survey of Plant No. was conducted on February 22, 1982 to assess the plant's ability to comply with EPA pretreatment regulations. A comparison with plant operation observed during the February 1980 survey (Table 4) revealed that the average water consumption had been reduced by 88.2 percent. These reductions were made possible primarily by the installation of an automatic plating machine and rinsewater flow restrictors. This machine now accounts for 80 percent of the plant's production.

Analytical results of the composite effluent sample show that the plant is operating out of compliance because of the cyanide concentration. Recommendations are presented to correct this situation with minor in-plant changes at a reasonable cost.

#### Data Evaluation

In order to calculate the effect of various pollution control techniques, it is necessary to know the volume of dragout per production unit. To determine this quantity, a dragout experiment was conducted on the rinse tank following the nickel plating tank. Starting with fresh water in the rinse tank, samples of the rinsewater were taken as racks were removed. These samples and one from the plating tank were analyzed for nickel content (Table 4). From this data, the average dragout was calculated to be 0.021 liters per rack. At a production rate of 180 racks per hour, 3.78 l/hr of nickel plating solution is lost in the following rinse tank. Consideration of recovery of this solution is discussed later. For purposes of calculation,

Table 4. Plant No. 10 Performance Comparison

Effluent Analysis

February 1980 - February 1982

| Parameter          | 2/80   | 2/82   | Applicable Regulations<br><10,000 gpd |                | Percent<br>Reduction |
|--------------------|--------|--------|---------------------------------------|----------------|----------------------|
|                    |        |        | Daily Max.                            | 4-D<br>Average |                      |
| Effluent Flow, gpd | 48,600 | 5,720  |                                       |                | 88.2                 |
| Analyses, mg/l     |        |        |                                       |                |                      |
| All Metals         | 14.0   | 19.44  | -                                     | -              | 83.6                 |
| CN <sub>t</sub>    | 10.7   | 10.6   | 5.0                                   | 2.7            | 88.3                 |
| Au                 | *      | <0.5   | -                                     | -              | -                    |
| Rh                 | *      | <0.5   | -                                     | -              | -                    |
| Ag                 | <0.01  | <0.01  | -                                     | -              | -                    |
| Cd                 | <0.01  | <0.01  | 1.2                                   | 0.7            | -                    |
| Cr <sub>t</sub>    | 0.69   | <0.05  | -                                     | -              | -                    |
| Cu                 | 4.92   | 3.87   | -                                     | -              | -                    |
| Ni                 | 6.90   | 14.0   | -                                     | -              | -                    |
| Pb                 | 0.008  | <0.001 | 1.2                                   | 0.7            | -                    |
| Zn                 | 1.50   | 1.57   | -                                     | -              | -                    |
| Sn                 | *      | <1.0   | -                                     | -              | -                    |

\*Not analyzed.

Dragout = 0.021 1/rack

this dragout rate (3.78 l/rh) is assumed constant for all other solutions.

#### SOURCES OF CYANIDE

An examination of the plating sequence (Figure 4) reveals three major sources of cyanide pollution. These are the rinse overflow streams following the copper strike, the cyanide activator, and the brass plating tanks. Based upon the dragout rate determined above and the cyanide concentration of each bath, the cyanide entering each rinse tank is calculated as shown in Table 6. The largest contributor of cyanide to rinsewater (57%) is the Cyanide Activator. Since the cyanide activator consists of 3.25 oz/gal of NaCN, a necessary constituent of the brass plating bath itself, the running rinse between the activator and brass plating tank serves no apparent purpose. In fact, its dragout into the plating bath progressively dilutes the bath. In addition, the overflow from this rinse contributes over half of the total cyanide in the plant effluent. It is recommended that the use of this rinse be discontinued.

The second practice in question is the use of the cyanide activator itself. Experience in other plating shops using similar brass plating bath composition has shown that the activator is necessary only if parts are permitted to dry before entering the plating bath. It is therefore recommended that the elimination of the activator be considered.

#### NICKEL LOSSES

Although nickel levels in effluent are not regulated for plants with under 10,000 gpd flow, the value of lost plating solution deserves consideration. Assuming all the nickel in the effluent (14.0 mg/l) originated in the rinse stream following the nickel plating tank, the nickel losses are calculated to be 8 gallons of plating solution in 8 hours of operation. At a \$4.00/gal

Table 5. Plant No. 10 Field Data - Dragout Experiment

Water Use:

251800 gal  
5720 gpd

Aug. 17 - Nov. 2, 1982 (44 work days)

Plating during visit: Cu, Ni, Au, Sn, brass

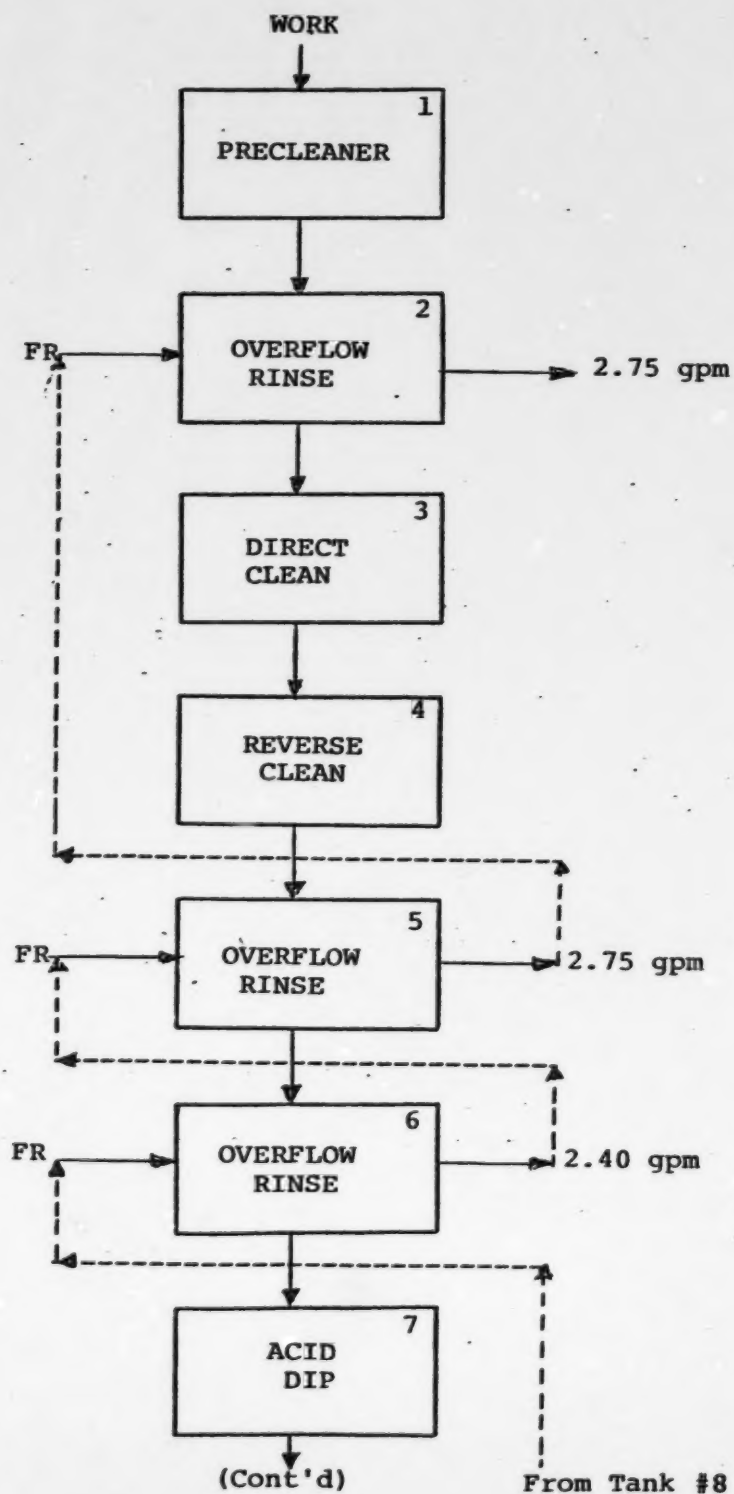
Dragout Experiment:

Used - Ni Dragout Tank on new Automatic Line  
Dim - 58" x 23" x 39" (LxWxD)

| Sample No. | Production Units | Ni Concentration, mg/l |
|------------|------------------|------------------------|
| 10 - DR1   | 0 racks          | 9.52                   |
| 10 - DR2   | 15 racks         | 47.2                   |
| 10 - DR3   | 42 racks         | 90.5                   |
| 10 - DR4   | 75 racks         | 70.4                   |
| 10 - DR5   | Ni Bath          | 32,500                 |

Calculated Dragout After 75 Racks = 0.021 l/rack.

Production Rate: 180 racks/hr.



PLANT #10

Figure 4 Automatic Plating Machine Process Sequence (Cont'd)

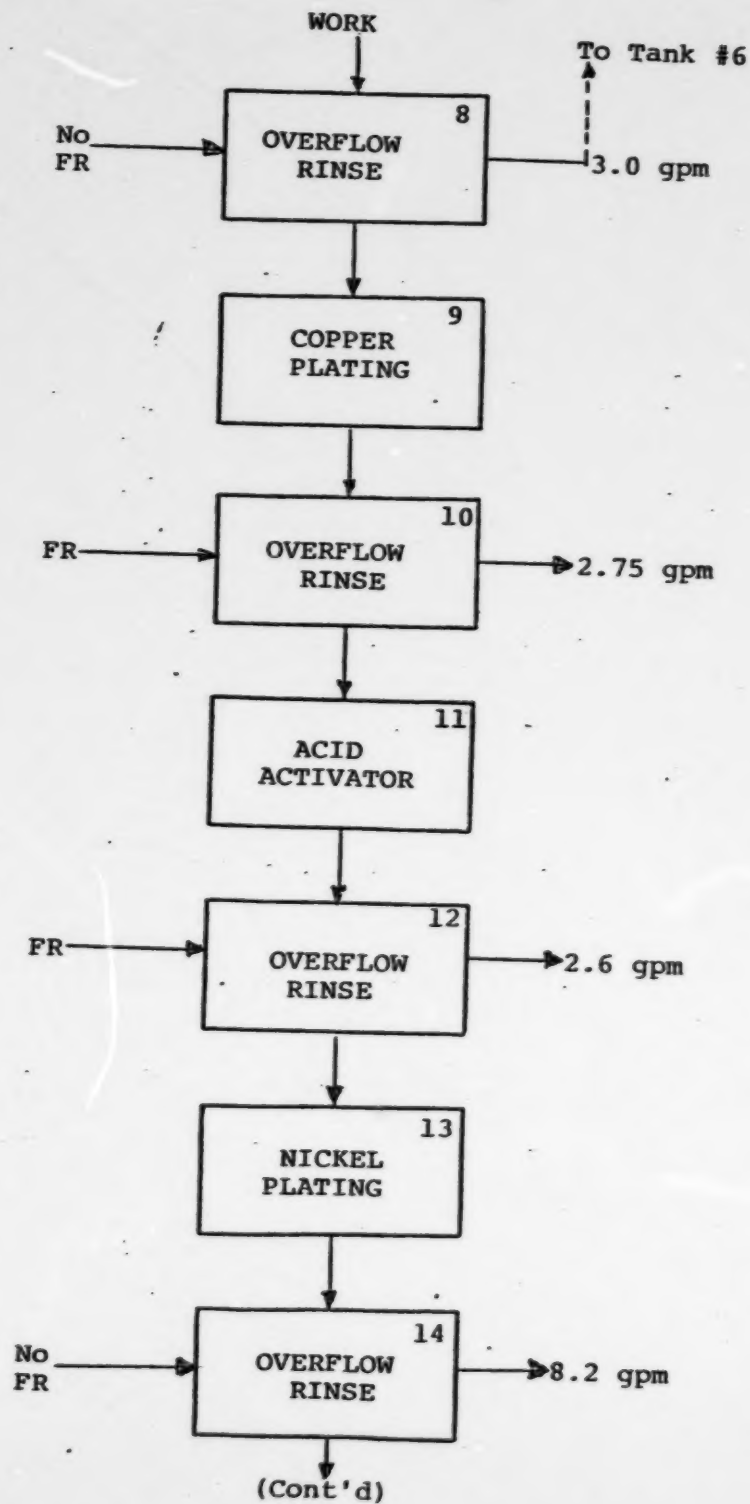
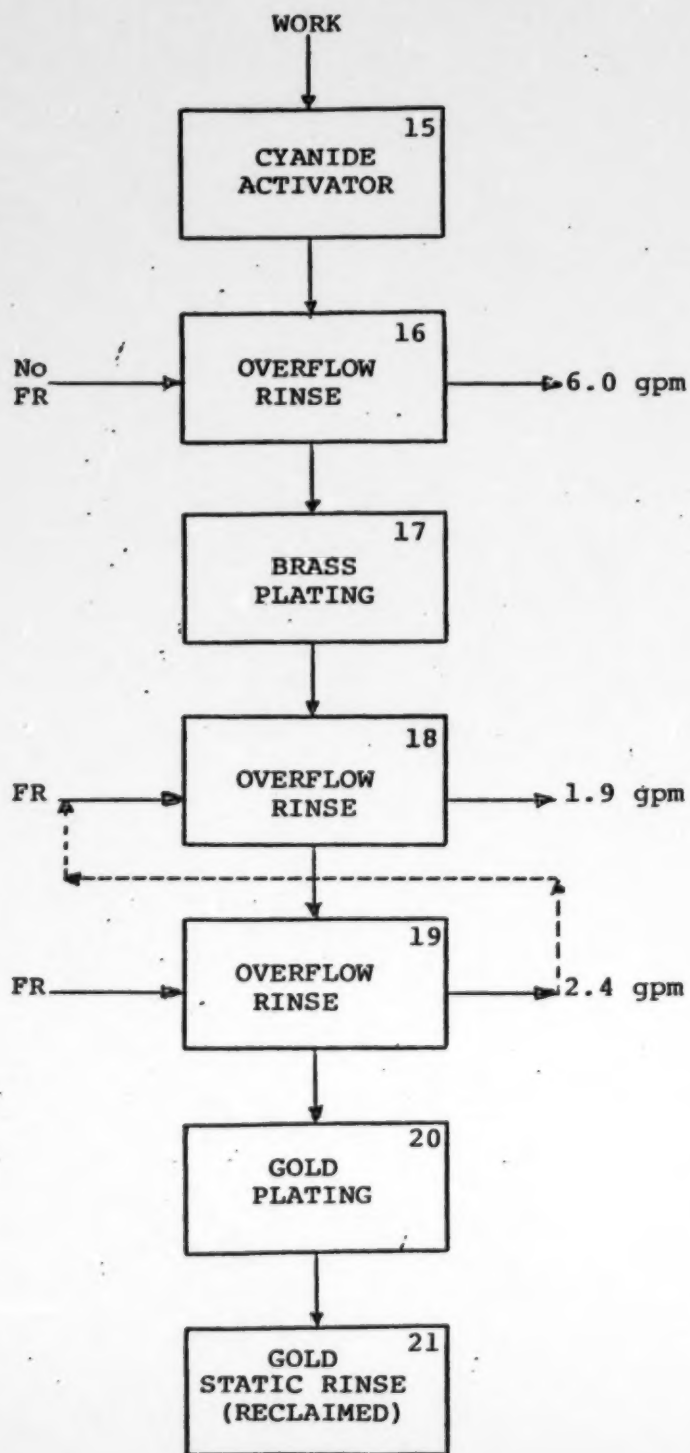


Figure 4 (Cont'd)



Note: Additional tanks not in use during survey.

Figure 4 (Cont'd)

NOTES

1. FR designates flow restrictor of aerating type.
2. Rinsewater flows shown were measured during the survey.
3. Dotted lines correspond to recommended water reduction and reuse piping. Pumps which may be required are not shown.

Figure 4 (Cont'd)

Table 6. Sources of Cyanide Pollution

| <u>Source</u> | <u>CN Concentration</u> | <u>mg CN/hr.</u> | <u>Percent of Total</u> |
|---------------|-------------------------|------------------|-------------------------|
| Cu Strike     | 1.25 oz/gal KCN         | 14,167           | 16.6                    |
| Brass Plating | 1.5 oz/gal NaCN         | 22,555           | 26.4                    |
| CN Activator  | 3.25 oz/gal NaCN        | 48,870           | 57.0                    |

cost (1982 dollars) for nickel plating solution, a loss of \$8,000/yr is sustained for 250 working days/yr. Prevention of this loss can justify recovery of the nickel solution through electrolytic or other means. If the cyanide activator and its rinse can be eliminated as suggested above, three tanks (counting the existing nickel rinse tank) will be available for utilization in nickel recovery. The first tank following nickel plating can be used as either a fog rinse or a dead rinse tank followed by two countercurrent rinses. Recovered nickel solution can be returned as makeup to the nickel plating tank.

#### WATER CONSERVATION

Although the average plant water consumption as taken from plant records over 44 working days was 5,720 gpd, measurements of rinse flows on the automatic machine recorded during the survey totaled 34.75 gpm, or 16,680 gpd for a full 8 hours of operation. If production requirements reach this level, maintaining the under-10,000-gpd status will become difficult with present rinse arrangements.

Repiping the running rinses following the reverse cleaner and brass plating in a countercurrent fashion will produce the same rinsing effect while saving much of the water currently consumed. Counterflow rinsing following nickel plating was discussed earlier. The overflow from the rinse following the acid dip tank can be reused to supply the reverse-clear counterflow rinses; and that overflow reused to supply the precleaner rinse. These water conservation measures are more expensive than other recommendations above because of the piping and pumps required. However, these measures will not be necessary until production demands force water consumption higher. Such expenditures will be more easily justified at that time.

## SUMMARY OF RECOMMENDATIONS FOR PLANT NO. 10

The following recommendations were presented for consideration.

1. Discontinue the running rinse following the cyanide activator.
2. Discontinue use of the cyanide activator itself.
3. Based upon the number of tanks made available through attempts to eliminate the activator, repipe tanks following nickel plating to utilize the most economical arrangement.

## ASSESSMENT OF CHANGES

Based upon the above recommendations, the first rinse tank following nickel plating (Tank No. 14, Figure 4) was converted to a still (dragout) tank during May 1982. The cyanide activator was simultaneously eliminated. During operation, the dragout tank solution was used to make up for evaporation in the nickel plating tank. After a period of time, staining was observed on parts leaving the brass plating tank. Because of production demands, the running rinse following nickel plating was reinstated. A mild acidic activator was substituted for the cyanide activator previously used. The staining problem ceased to exist. The overflow rinse following the activator (Tank No. 16) was sampled on July 29, 1983. Analysis revealed a concentration of  $<0.02$  mg/l of cyanide. This stream previously contributed 57 percent of the cyanide in the plant effluent (Table 6). At this writing, it is planned to again use the nickel dragout tank arrangement. It is felt that the new activator has solved the staining problem.

Plans call for repiping of rinses as recommended (by the dotted lines in Figure 4) in the near future. Installation of equipment for handling of batch dumps will also be required. Guidance for design of such a system is provided in Appendix C.

## REFERENCES

1. Federal Register, July 15, 1983.
2. Comfort, E., D. Harrison and D. Sherman, "Group Treatment Evaluation for Metal Finishers", EPA-600/82-81-143, September 1981.
3. Salomon, E., and E. Comfort, "Group Treatment-Options and Economics," Proceedings of the Third EPA/AES Conference on Advanced Pollution Control for the Metal Finishing Industry", Kissimmee, FL, April 14-16, 1980.

APPENDIX A

1982 ANALYTICAL RESULTS OF PLANT SURVEY  
(Huntington Industrial Park)

FEBRUARY 1982

ANALYTICAL RESULTS: PLANT #1  
(March 1982)

| CAS No. | Description           | Cyanide<br>(mg/l) | Au<br>(mg/l) | Rh<br>(mg/l) | Ag<br>(mg/l) | Od<br>(mg/l) | Cr<br>(mg/l) | Cu<br>(mg/l) | Ni<br>(mg/l) | Pb<br>(mg/l) | Zn<br>(mg/l) | Sn<br>(mg/l) |
|---------|-----------------------|-------------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|
| 23292   | Tap water<br>No. 01-1 |                   |              |              | <0.01        | <0.01        | <0.05        | <0.01        | <0.10        | <0.001       | <0.01        | <1.0         |
| 23293   | 01-FEM                |                   | <0.5         | <0.5         | 0.05         | <0.01        | 0.22         | 1.04         | 2.56         | 0.007        | 0.17         | <1.0         |
| 23294   | 01-FECN               | 0.14              |              |              |              |              |              |              |              |              |              |              |
| 23295   | Initial-01-DR-1       |                   |              |              |              |              |              |              | 0.16         |              |              |              |
| 23296   | 30 racks-01-DR-2      |                   |              |              |              |              |              |              | 483          |              |              |              |
| 23297   | 60 racks-01-DR-3      |                   |              |              |              |              |              |              | 579          |              |              |              |
| 23298   | 90 racks-01-DR-4      |                   |              |              |              |              |              |              | 1200         |              |              |              |
| 23299   | Bath-01-DO-5          |                   |              |              |              |              |              |              | 31800        |              |              |              |

Method of Analysis: Federal Register, Vol. 41, No. 232  
1 December 1976

ANALYTICAL RESULTS: PLANT #4  
(March 1982)

| CAS No. | Description               | Cyanide<br>(mg/l) | Au<br>(mg/l) | Rh<br>(mg/l) | Ag<br>(mg/l) | Cd<br>(mg/l) | Cr<br>(mg/l) | Cu<br>(mg/l) | Ni<br>(mg/l) | Pb<br>(mg/l) | Zn<br>(mg/l) | Sn<br>(mg/l) |
|---------|---------------------------|-------------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|
| 23300   | 04 FEM                    |                   | <0.5         | <0.5         | <0.01        | <0.01        | <0.05        | 0.33         | 0.70         | 0.006        | 0.06         | <1.0         |
| 23301   | 04 FECN                   | 0.60              |              |              |              |              |              |              |              |              |              |              |
| 23302   | 04-DR-1-Initial           |                   |              |              |              |              |              |              |              |              |              |              |
| 23303   | 10 racks-04-DR-2          |                   |              |              |              |              |              |              | 0.16         |              |              |              |
| 23304   | 27 racks-04-DR-3          |                   |              |              |              |              |              |              | 26.7         |              |              |              |
| 23305   | 40 racks-04-DR-4          |                   |              |              |              |              |              |              | 20.6         |              |              |              |
| 23306   | 04-DR-5                   |                   |              |              |              |              |              |              | 124          |              |              |              |
| 23307   | Spl Fore dragout<br>study |                   |              |              |              |              |              |              | 28100        |              |              |              |
|         |                           |                   |              |              |              |              |              |              |              |              |              | 1.23         |

Method of Analysis: Federal Register, Vol. 41, No. 232  
1 December 1976

ANALYTICAL RESULTS: PLANT #10  
(March 1982)

| CAS No. | Description               | Cyanide<br>(mg/l) | Au<br>(mg/l) | Rh<br>(mg/l) | Ag<br>(mg/l) | Cd<br>(mg/l) | Cr<br>(mg/l) | Cu<br>(mg/l) | Ni<br>(mg/l) | Pb<br>(mg/l) | Zn<br>(mg/l) | Sn<br>(mg/l) |
|---------|---------------------------|-------------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|
| 23385   | Final Effluent<br>10-FEM  |                   | <0.5         | <0.5         | <0.01        | <0.01        | <0.05        | 3.87         | 14.0         | <0.001       | 1.57         | <1.0         |
| 23386   | Final Effluent<br>10-FECN | 10.6              |              |              |              |              |              |              |              |              |              |              |
| 23387   | Rack Plating<br>10-DR-1   |                   |              |              |              |              |              |              | 9.52         |              |              |              |
| 23388   | Rack Plating<br>10-DR-2   |                   |              |              |              |              |              |              | 47.2         |              |              |              |
| 23389   | Rack Plating<br>10-DR-3   |                   |              |              |              |              |              |              | 90.5         |              |              |              |
| 23390   | Rack Plating<br>10-DR-4   |                   |              |              |              |              |              |              | 70.4         |              |              |              |
| 23391   | Rack Plating<br>10-DR-5   |                   |              |              |              |              |              |              | 32500        |              |              |              |

Method of Analysis: Federal Register, Vol. 41, No. 232  
1 December 1976



CENTEC ANALYTICAL SERVICES, INC.  
A SUBSIDIARY OF THE CENTEC CORPORATION

P. O. BOX 956  
2160 INDUSTRIAL DRIVE  
SALEM, VIRGINIA 24153  
(703) 387-3995

— ANALYTICAL RESULTS REPORT —

Mr. Don Harrison  
CENTEC Corporation  
Centec Building  
11200 Roger Bacon Drive  
Reston, Virginia 22090

Re: Water Analysis  
CAS Commission No. 520

REPORT DATE/NUMBER: 29 March 1982/3

SAMPLES COLLECTED: 23 March 1982/0700 to 1500

BY: Erich Salomon

SAMPLES RECEIVED AT LAB: 26 March 1982/0930

ANALYSIS FOR: Oils and Grease (O&G), pH, Total Suspended  
Solids (TSS)

METHOD OF ANALYSIS: Re: Federal Register, Vol. 41, No. 232  
1 December 1976

| CAS No. | Description                  | O&G (mg/l) | pH  | TSS (mg/l) |
|---------|------------------------------|------------|-----|------------|
| 23846   | Plant #1<br>15 min intervals | 6          | 4.0 | 4          |

If you have any questions or comments concerning this report,  
please do not hesitate to contact us.

Prepared by:

CENTEC ANALYTICAL SERVICES

David F. Tompkins  
Chemist

DFT:msh



SEP 10 REC'D

P. O. BOX 956  
2160 INDUSTRIAL DRIVE  
SALEM, VIRGINIA 24153  
(703) 387-3995

— ANALYTICAL RESULTS REPORT —

Mr. Don Harrison  
CENTEC Corporation  
Centec Building  
11260 Roger Bacon Drive  
Reston, Virginia 22090

Re: Water Analysis  
CAS Commission No. 520

REPORT DATE/NUMBER: 09 September 1982/4

SAMPLES COLLECTED: 29 July 1982 Plant #10

BY: D. Harrison

SAMPLES RECEIVED AT LAB: 02 August 1982; 0845

ANALYSIS FOR: Cyanide and Nickel (Ni)

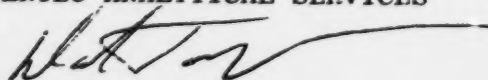
METHOD OF ANALYSIS: Re: Federal Register, Vol. 41, No. 232  
1 December 1976

| CAS Number | Description     | Cyanide<br>(mg/l) | Ni<br>(mg/l) |
|------------|-----------------|-------------------|--------------|
| 25598      | Nickel Rinse    |                   | 18.1         |
| 25599      | Activator Rinse | <0.02             |              |

If you have any questions or comments concerning this report,  
please do not hesitate to contact us.

Prepared by:

CENTEC ANALYTICAL SERVICES

  
David F. Tompkins  
Chemist

DFT/mls

APPENDIX B

1980 ANALYTICAL RESULTS OF PLANT SURVEY  
(Huntington Industrial Park)

FEBRUARY 1982

**ANALYTICAL RESULTS: PLANT #1**  
(March 1980)

| CAS No. | Description    | Date Received    | Ag (mg/l) | Cr+6 (mg/l) | CN-T (mg/l) | CN-A (mg/l) | Cd (mg/l) | Cr (mg/l) | Cu (mg/l) | Fe (mg/l) | Ni (mg/l) | Pb (mg/l) | Zn (mg/l) |
|---------|----------------|------------------|-----------|-------------|-------------|-------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| 9881    | CN Bath Comp.  | 2/13/80;<br>1515 |           |             | 20.4        | 18.1        |           |           |           |           |           |           |           |
| 9883    | CN Bath Comp.  | 2/13/80;<br>1515 |           | <0.10       |             |             | 0.03      | <0.05     | 6.85      | 0.42      | 0.25      | 0.008     | 0.82      |
| 9878    | Final Effluent | 2/13/80;<br>1515 | <0.01     | <0.10       |             |             | <0.01     | 0.05      | 0.68      | 0.07      | 0.95      | <0.001    | 0.06      |
| 9879    | Final Effluent | 2/13/80;<br>1515 |           |             | 2.9         | 2.2         |           |           |           |           |           |           |           |
| 9928    | Electro-Clean  | 2/15/80;<br>1330 |           | <0.10       |             |             | 0.13      | 0.20      | 4.00      | 1.73      | 1.72      | 1.00      | 1.15      |
| 9929    | Ultra-Sonic    | 1/15/80;<br>1330 |           | <0.10       |             |             | 0.92      | 0.20      | 10.2      | 1.54      | 6.35      | 1.00      | 1.15      |
| 9930    | Acid Rinsing   | 1/15/80;<br>1330 |           | <0.10       |             |             | 0.21      | 0.06      | 9.95      | 22.5      | 1.90      | 0.50      | 1.75      |
| 9942    | Grab           | 1/17/80;<br>1830 |           | <0.10       | 3520        | 1120*       | <0.01     | 0.27      | 0.05      | 855       | 0.35      | 0.008     | 0.10      |

\* Point of chlorination was not actually reached due to nature of sample.

Method of Analysis: Federal Register, Vol. 41, No. 232.1  
1 December 1976

Prepared by:

CENTEC ANALYTICAL SERVICES

*Jed R. Robinson*

Ted L. Robinson, Chemist

# CENTEC ANALYTICAL SERVICES, INC.

A SUBSIDIARY OF CENTEC, INC.  
OFFICES IN RESTON, VA • FORT LAUDERDALE, FLA

P.O. BOX 956  
8160 INDUSTRIAL DRIVE  
SALEM, VIRGINIA 24153  
(703) 387-3905

## — ANALYTICAL RESULTS REPORT —

Mr. John Kresky  
CENTEC Corporation  
11800 Sunrise Valley Drive  
Reston, VA 22091

Re: Plant #4  
CAS Commission No. 2907-02

REPORT DATE/NUMBER: 11 March 1980/4

TYPE OF SAMPLES: Industrial Wastewater

SAMPLES COLLECTED BY: CAS/ISCO

ANALYSIS FOR: Cyanide, Total (CN-T), Cyanide, Amenable to Chlorination (CN-A), Cadmium (Cd), Chromium (Cr), Copper (Cu), Iron (Fe), Nickel (Ni), Lead (Pb), Zinc (Zn), Chromium +6 Silver (Ag)

METHOD OF ANALYSIS: Re: Federal Register, Vol. 41, No. 232, 1 Dec.. 1976

| CAS No. | Description    | Date Received       | CN-T (mg/l) | CN-A (mg/l) | Cd (mg/l) | Cr (mg/l) | Cu (mg/l) |
|---------|----------------|---------------------|-------------|-------------|-----------|-----------|-----------|
| 9884    | CN Rinse Bath  | 2/13/80;<br>2/12/80 | 8.6         | 8.6         | <0.01     | <0.05     | 0.06      |
| 9985    | Final Effluent | 2/13/80;<br>2/12/80 | 3.9         | 3.9         | <0.01     | <0.05     | 0.45      |

| CAS No. | Description    | Fe (mg/l) | Ni (mg/l) | Pb (mg/l) | Zn (mg/l) | Cr+6 (mg/l) | Ag (mg/l) |
|---------|----------------|-----------|-----------|-----------|-----------|-------------|-----------|
| 9884    | CN Rinse Bath  | <0.10     | <0.10     | <0.001    | <0.01     | <0.10       |           |
| 9885    | Final Effluent | <0.10     | 1.10      | 0.004     | 0.17      | <0.10       | 0.13      |

Prepared by:

CENTEC ANALYTICAL SERVICES

*Ted L. Robinson*

Ted L. Robinson  
Chemist

TLR/lsm

SAMPLING AND ANALYSIS INCLUDING TO: WASTEWATER/TREATMENT • WATER/DRINKING WATER • BIOLOGICAL MONITORING • CYBER COMPLIANCE • AIR QUALITY • TOXIC SUBSTANCES

# CENTEC ANALYTICAL SERVICES, INC.

A SUBSIDIARY OF CENTEC INC.  
OFFICES IN RESTON, VA • FORT LAUDERDALE, FLA

P.O. BOX 956  
8160 INDUSTRIAL DRIVE  
SPRING, VIRGINIA 22153  
(703) 387-3005

## — ANALYTICAL RESULTS REPORT —

Mr. John Kresky  
CENTEC Corporation  
11800 Sunrise Valley Drive  
Reston, VA 22091

Re: Plant #10  
CAS Commission No. 2907-02

REPORT DATE/NUMBER: 11 March 1980/8

TYPE OF SAMPLES: Industrial Wastewater

SAMPLES COLLECTED BY: ISCO

ANALYSIS FOR: Cyanide, Total (CN-T), Cyanide, Amenable to Chlorination (CN-A), Cadmium (Cd), Chromium (Cr), Copper (Cu), Iron (Fe), Nickel (Ni), Lead (Pb), Chromium +6, Zinc (Zn), Silver (Ag)

METHOD OF ANALYSIS: Re: Federal Register, Vol. 41, No. 232, 1 Dec. 1976

| CAS No. | Description               | Date Received    | CN-T (mg/l) | CN-A (mg/l) | Cd (mg/l) | Cr (mg/l) | Cu (mg/l) |
|---------|---------------------------|------------------|-------------|-------------|-----------|-----------|-----------|
| 9924    | Final Effluent<br>2/14/80 | 2/15/80;<br>1330 | 10.7        | 7.7         | <0.01     | 0.69      | 4.92      |
| 9925    | CN Rinse Bath<br>2/14/80  | 2/15/80;<br>1330 | 56.6        | 52.2        | <0.01     | <0.05     | 16.8      |

| CAS No. | Description    | Fe (mg/l) | Ni (mg/l) | Pb (mg/l) | Zn (mg/l) | Cr+6 (mg/l) | Ag (mg/l) |
|---------|----------------|-----------|-----------|-----------|-----------|-------------|-----------|
| 9924    | Final Effluent | 1.10      | 6.90      | 0.008     | 1.50      | <0.10       | <0.01     |
| 9925    | CN Rinse Bath  | 0.07      | 6.45      | <0.001    | 5.20      | <0.10       |           |

Prepared by:

CENTEC ANALYTICAL SERVICES

*Ted L. Robinson*  
Ted L. Robinson  
Chemist

TLR/lsm

APPENDIX C  
GUIDELINES FOR BATCH TREATMENT  
OF DUMP SOLUTIONS

## HANDLING BATCH DUMPS

### Introduction

Plating shops which operate in compliance during normal operation are still faced with the disposal of depleted acid and caustic cleaning solutions as well as spent or contaminated plating solutions. The dump solutions and the best disposal method will vary from shop to shop.

### Chemistry of Treatment

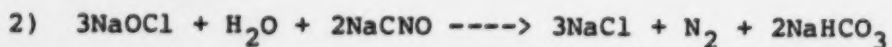
Batch dump solutions are usually unacceptable for direct sewer discharge because:

- o They may contain cyanides which must be destroyed prior to discharge.
- o They may contain chromium in the hexavalent state ( $\text{Cr}^{+6}$ ) which must be reduced to trivalent chrome ( $\text{Cr}^{+3}$ ) prior to discharge.
- o They are caustic or acidic, having a pH outside the allowable discharge limits.

Solutions containing cyanides or hexavalent chromium must be treated with purchased chemicals to destroy the cyanides and reduce the chromium. Adjustment of pH to within allowable limits can often be accomplished by combining waste solutions.

### Oxidation of Cyanides

Cyanides are destroyed in wastes by oxidation with an oxidizing agent (sodium hypochlorite) and an alkali (sodium hydroxide). When oxidized with sodium hypochlorite, the cyanides are either partially destroyed to the less toxic cyanates, or completely destroyed to non-toxic nitrogen gas and carbon dioxide. The reactions showing the oxidation of cyanide with sodium hypochlorite are:



Step No. 1 is a reaction dependent upon pH. At pH values below 8.0, the oxidation is never completed. At pH 10.0 or above and with the proper alkali requirements, the cyanide is completely converted to the much less toxic sodium cyanate within a matter of minutes.

The second step, oxidation of the cyanate to nitrogen and carbon dioxide (as bicarbonate), is likewise dependent upon pH and is accelerated by a decreasing pH. At pH 8.5, about 20 to 25 minutes are required for the reaction to go to completion.

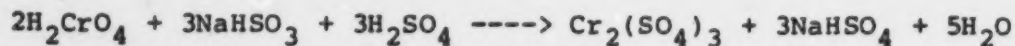
In practice, the destruction of cyanide requires about 7.5 parts of sodium hypochlorite per part of cyanide.

Recently, electrolytic units for the destruction of concentrated cyanide solutions have become commercially available. The cyanide solution is continuously circulated through the electrolytic unit until the cyanides are completely destroyed. Operating costs are limited to the electricity to power the unit.

### Reduction of Hexavalent Chromium

Hexavalent chromium is reduced to the trivalent state by the addition of sodium bisulfite in the presence of sulfuric acid.

The reaction for chromate treatment is:



(Sodium bisulfate is usually prepared by dissolving sodium metabisulfate,  $\text{Na}_2\text{S}_2\text{O}_3$ , in water to produce the treatment solution.)

The speed of the reduction reaction is dependent upon pH. The reaction is nearly instantaneous at pH 2.5. Sulfuric acid is used to maintain the required pH. A noticeable color change from yellow or brown to blue-green occurs as the reaction proceeds.

In practice about three parts of sodium bisulfite and two parts of sulfuric acid are required to reduce one part of hexavalent chromium.

### Adjustment of pH

The periodic dumping of depleted acids and caustic cleaners to the sewer is a familiar operation in plating shops. Limitations of plant effluent of 5.5 to 10.5 pH imposed on plants discharging to the sewer system prohibit this practice.

Acids and caustics can be combined prior to dumping, thereby neutralizing one another. The volume of spent cleaner required to neutralize a given quantity of spent acid can be quickly

determined by titrating a measured quantity of acid with cleaner solution until the pH is within discharge limitations. The plot of such a titration is shown in Figure C-1. In this case 30 ml of soak cleaner solution was required to bring 25 ml of electro-acid to a pH of 8.0. Therefore, 270 gallons of the cleaner would be required to raise 225 gallons of acid to a pH of 8.0 ( $225 \times 30/25 = 270$ ). If insufficient waste cleaner were available, the pH adjustment would have to be completed with the addition of purchased caustic. If temporary storage tanks are provided for the depleted acid and caustic solutions, these solutions can be used for adjusting pH and the quantity of purchased treatment chemicals can be kept to a minimum.

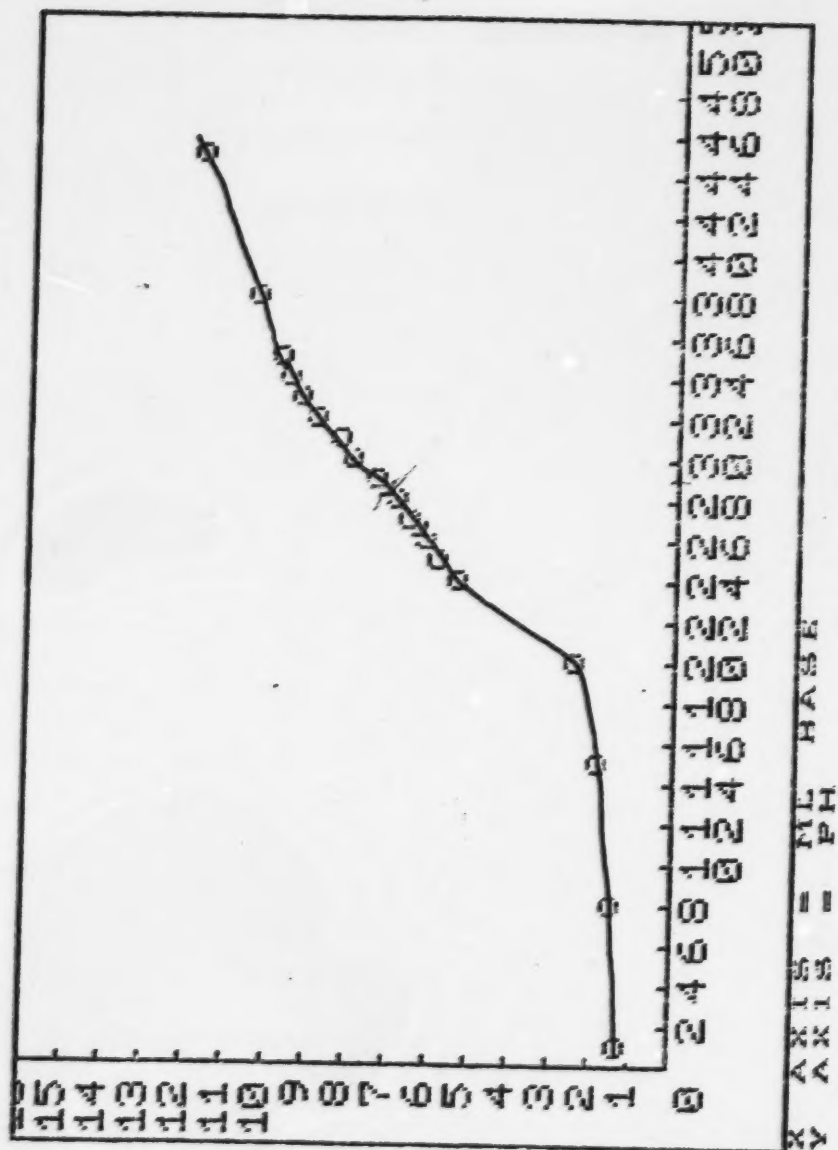
#### SYSTEM DESIGN

A system designed to treat batch dumps prior to discharge is shown in Figure C-2. Since the requirements of each plating shop are different, a discussion of the various components will aid in developing specific requirements.

##### Treatment/Storage Tanks

Tanks purchased for storage or treatment of solutions should be made of non-metallic material such as polyethylene, polypropylene, fiber-glass reinforced plastics (FRP), etc. The size of the tank should be large enough to accommodate the largest dump expected at any one time. It is wise to allow 25-50 percent additional tank capacity to prepare for an unexpected dump. Treatment tanks must be large enough to hold the batch to be treated plus the volume of treatment chemicals required.

Figure C-1 TITRATION CURVE  
SOAK CLEANER/25 ML ELECTRO ACID



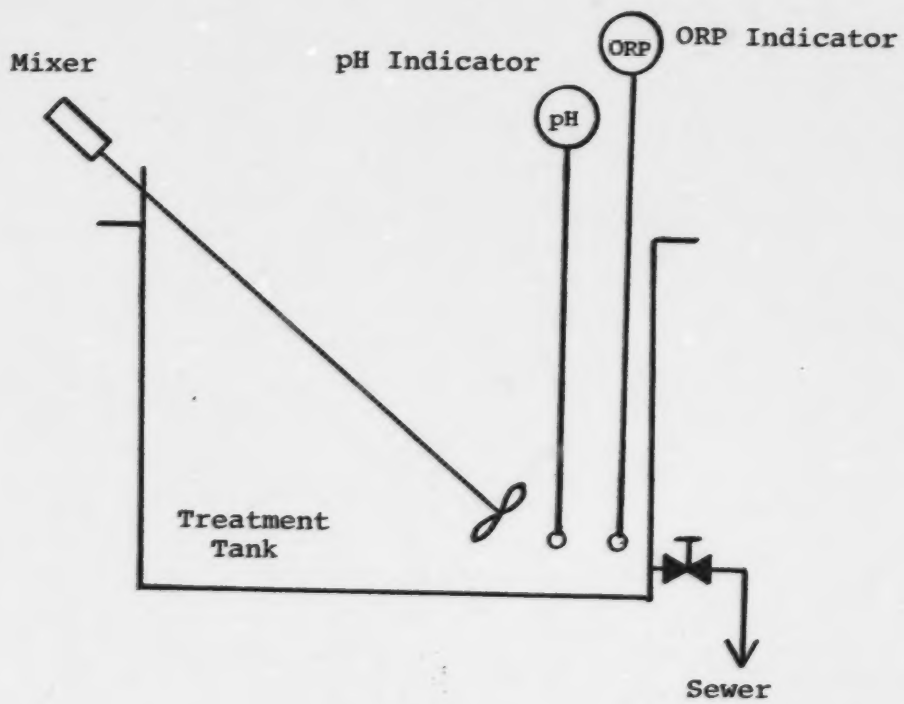


Figure C-2 Simplified Batch Treatment System

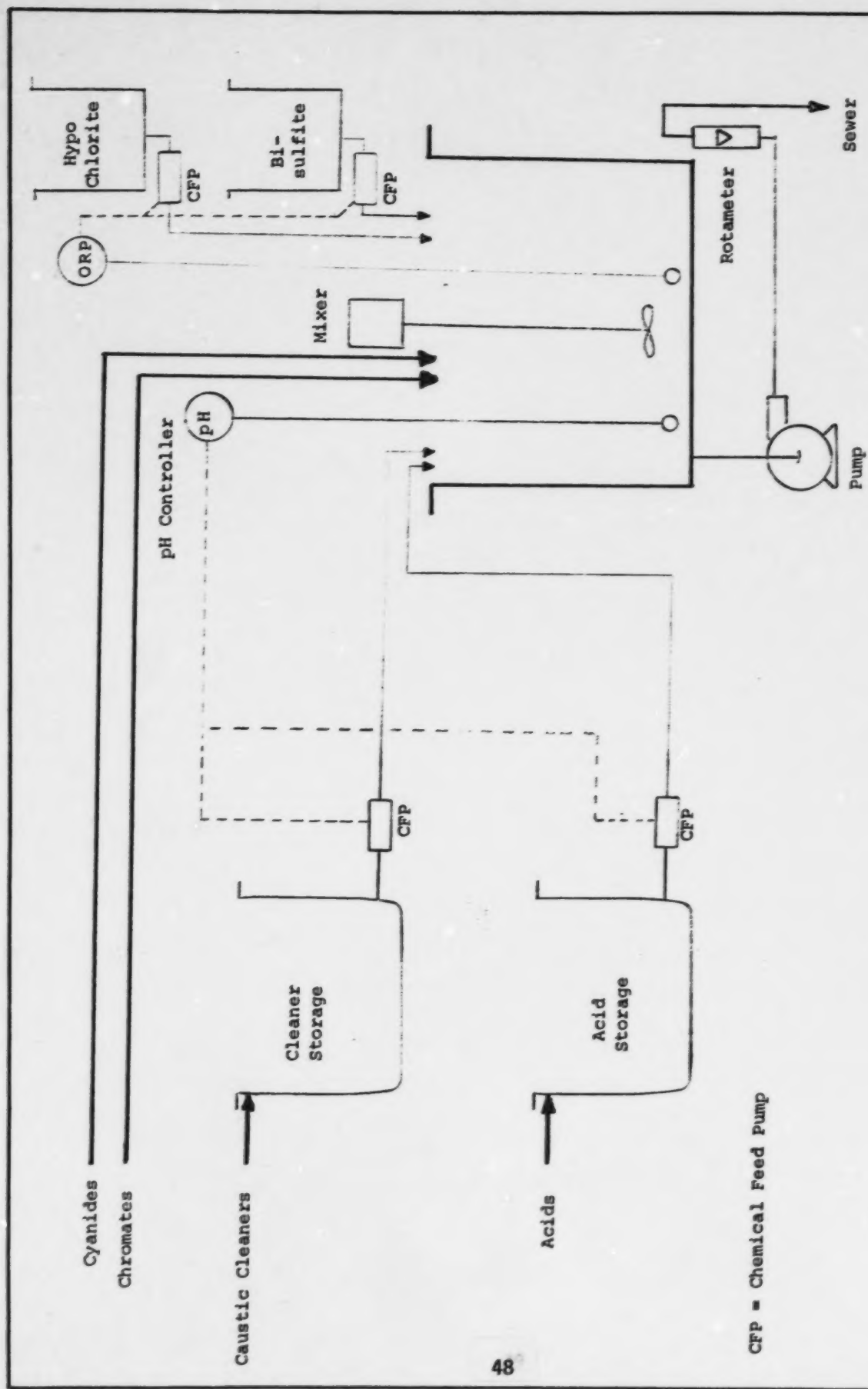


Figure C-3 Semi-Automatic Batch Treatment System

### Solution Transfer

The most economical collection system for handling dump solutions depends upon dump volumes and frequency. Solutions such as chromate dips are generally of small volume and infrequently dumped. These can be transferred to drums and moved to the treatment area by forklift or handtruck. Cleaners and acid dips may be more easily handled in a piped system to the treatment area because of their volume and dump frequency. It should be remembered that cyanides must be segregated from all other solutions to avoid possible contact with acidic solutions.

### Instrumentation

Two basic measurements are required in the treatment of plating wastewater; pH and Oxidation-Reduction Potential (ORP). The measurement of pH is accomplished through the use of a glass electrode sensor. The electrode is normally submerged in the liquid being measured and must be kept wet at all times. A temperature compensating probe is also required since the pH measurement varies with the solution temperature. The probes are commonly supplied in the same holder. The signal from the probe is connected to an indicator (Figure C-1) which displays the reading in pH units. Ranges of 0-14 or 2-12 pH units are common. The meter reading is used as a guide for caustic addition to raise the pH or acid addition to lower the pH. For automatic addition of chemicals (Figure C-3) an indicator controller is used to cycle chemical feed pumps to attain the desired pH. A single controller can be used to control both acid addition and caustic addition to control the pH within a given range. Instruments for pH measurement and control can be supplied by most major instrument manufacturers.

The measurement of ORP, sometimes called REDOX, is also accomplished with a

probe but of different design. In this case, a fine wire is embedded in glass to make contact with the solution. A gold wire is used if measurement of cyanide oxidation reactions is required. The ORP reading gives an indication that the reaction has reached completion. As in the case of pH measurements, the instrument can be purchased as either an indicator or an indicator controller. The controller version cycles the chemical feed pump to attain the desired reading. In Figure C-3 the operator must manually select the required feed pump depending upon the treatment desired, i.e., hypochlorite would be required for cyanide oxidation; bisulfite for chromium reduction.

#### Chemical Feed Pumps

Chemical feed pumps are available in a wide variety of designs and vary considerably in price. Most are diaphragm type pumps. The most simple design pumps chemicals at a fixed rate. The pump is turned on and off by a controller to meet the reaction demand. More sophisticated designs have provisions for varying the flow rate of the chemical.

#### Flow Meters

It is often desirable to measure the flow of the treated solution in order to control the rate it is fed into the plant's effluent stream. A manual throttling valve followed by a rotameter serves this purpose.